Synthesis, Structure, and Isomerisation of Triruthenium and Triosmium Clusters derived from 3-Dimethylaminoprop-1-yne; *X*-Ray Crystal Structure of $[Ru_3{}^-H(CO)_9(Me_2N^+{=}C^-C{=}CH_2)]$ †

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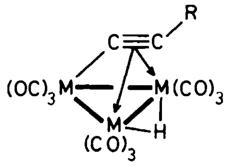
Both $[Ru_3(CO)_{12}]$ and $[Os_3(CO)_{12}]$ react with 3-dimethylaminoprop-1-yne ($HC{\equiv}CCH_2NMe_2$) to give fairly low yields of the compounds $[M_3H(CO)_9(Me_2NCCCH_2)]$ (M = Ru or Os), apparently derived by oxidative addition with cleavage of the terminal C–H bond and a 1,3 shift of the NMe_2 group. Crystals of $[Ru_3H(CO)_9(Me_2NCCCH_2)]$ are monoclinic, space group $P2_1/n$ with $Z = 4$ and cell dimensions $a = 13.067(2)$, $b = 10.398(2)$, $c = 15.544(2)$ Å, and $\beta = 112.78(2)°$; the *X*-ray structure was refined to $R = 0.019\,8$ for 3 138 observed reflections. The μ_3 ligand is not bound like the μ_3-allenyl ligand in $[Ru_3H(CO)_9(\mu_3\text{-}EtC{=}C{=}CHMe)]$ but extensive π donation from the NMe_2 group modifies the ligand-to-metal bonding and makes a zwitterionic description $[Ru_3{}^-H(CO)_9(Me_2N^+{=}C{-}C{=}CH_2)]$ more realistic. In spite of the different bonding, the terminal CH_2 protons of the triruthenium compound exchange (n.m.r. coalescence), corresponding to the methyl exchange previously observed for $[Ru_3H(CO)_9(\mu_3\text{-}MeC{=}C{=}CMe_2)]$. The triruthenium compound much less readily undergoes a hydrogen-atom shift observed generally for compounds of type $[Ru_3H(CO)_9(R^1C{=}C{=}CHR^2)]$, being stable up to at least 140 °C. However, a PPh_3-catalysed shift is observed at 55 °C to give $[Ru_3H(CO)_9(Me_2NCCHCH)]$ as well as the substitution product $[Ru_3H(CO)_8(PPh_3)(Me_2NCCCH_2)]$.

Functionalisation of alkynes might be expected to modify the way they react with $[Ru_3(CO)_{12}]$ or $[Os_3(CO)_{12}]$. Simple unfunctionalised alkynes react in various ways with these clusters but three types of trinuclear derivatives have been obtained predominantly; compounds of type (1) have been obtained from terminal alkynes but internal alkynes lead to compounds of types (2) and (3).[1] Compounds (1)—(3) are derived by oxidative addition with cleavage of C–H bonds, compound (3) being formed from (2) by isomerisation. With hydroxyalkynes the chemistry may be significantly modified. Although compounds of type (1) are obtained with R = CMe_2OH, CPh_2OH, CH_2CH_2OH, *etc.*, and have almost the same structure as when R is an alkyl group, the hydroxy-function modifies their reactivity. Thus when R = CPh_2OH there is a facile acid-catalysed isomerisation with hydroxide transfer from carbon to metal to give $[M_3H(CO)_9(OH)(C{=}C{=}CPh_2)]$ [2] and when R = CH_2CH_2OH cyclisation by an intramolecular nucleophilic attack leads to $[Os_3H_2(CO)_9(\mu_3\text{-}\overline{C{=}CCH_2CH_2O})]$.[3] In spite of these differences in reactivity, the introduction of hydroxide groups appears to have negligible consequence on the structures of the clusters. Compounds (1; M = Ru, R = CMe_2OH)[4] and (3; R^1 = H, R^2 = OH)[5] have metal frameworks and metal-carbon bonding indistinguishable from those found for simple hydrocarbon ligands. This might not be the case on introducing dialkylamino-groups. For example, Shapley *et al.*[6] have shown that replacement of a hydrogen atom in $[Os_3H(CO)_{10}(\mu\text{-}CH{=}CH_2)]$ by NEt_2 does not give compound (4) but rather the zwitterionic molecule (5). The better donor properties of dialkylamino- compared with hydroxy-groups and the ability of the metal clusters to accommodate negative charge led us to expect effects like those observed by Shapley *et al.*[6] on introducing dialkylamino-groups into compounds (1)—(3).



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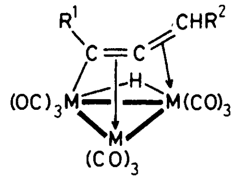

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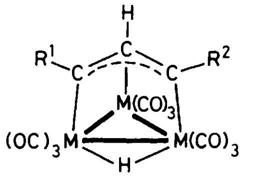

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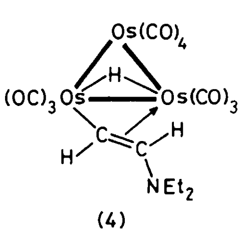

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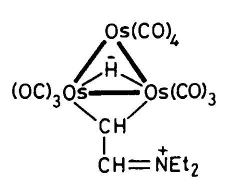

(5)

We have already noted some n.m.r. effects resulting from π donation from NMe_2 groups in ruthenium clusters derived from $MeC{\equiv}CCH_2NMe_2$ [7] and we now describe the synthesis and characterisation of triruthenium and triosmium derivatives

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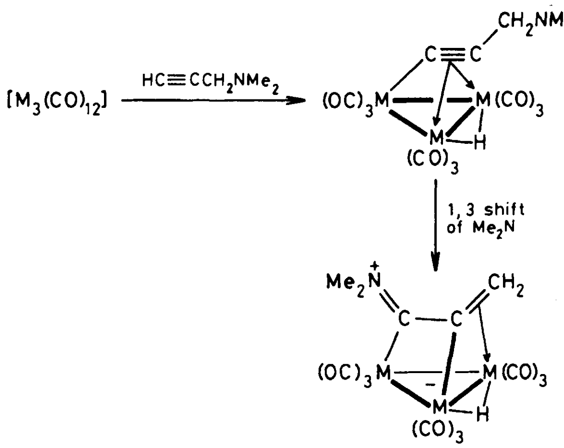
† *Supplementary data available* (No. SUP 23972, 23 pp.): bond lengths and angles, H-atom co-ordinates, thermal parameters, structure factors. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

Table 1. Spectroscopic data for new compounds

Compound	$\nu(CO)$ [a]/cm^{-1}	^1H N.m.r. [b] δ/p.p.m.	Assignment	Coupling constant/Hz
(6) $[Ru_3H(CO)_9(Me_2NCCCH_2)]$ [c]	2 084m, 2 055vs, 2 036vs, 2 013s, 2 009s, 1 998m, 1 989m, 1 961w	2.25(m)	CH	
		2.12(m)	CH	
		2.57(s)	NMe	
		2.88(s)	NMe	
		−23.25(d)	RuH	J 2.7
(7) $[Os_3H(CO)_9(Me_2NCCCH_2)]$ [d]	2 085m, 2 055s, 2 033s, 2 010s, 2 001m, 1 991m, 1 975ms, 1 970m, 1 949m	2.86(s)	CH	
		1.66(s)	CH	
		2.64(s)	NMe	
		2.43(s)	NMe	
		−19.80(s)	OsH	
(11) $[Ru_3H^a(CO)_9(Me_2NCCH^bCH^c)]$	2 088s, 2 066ms, 2 060vs, 2 032vs, 2 017s, 2 005s, 1 994s, 1 975s, 1 957w	6.03(dd)	CH^b	J_{ab} 2.5
		8.20(d)	CH^c	J_{bc} 8.0
		3.23(s)	NMe	
		3.50(s)	NMe	
		−18.50(d)	RuH^a	
(12) $[Ru_3H^a(CO)_8(PPh_3)(Me_2NCCCH_2)]$	2 068s, 2 034vs, 2 012m, 2 001vs, 1 977m, 1 958m, 1 943w	2.73(m)	CH_2	
		3.40(s)	NMe	
		3.51(s)	NMe	
		−18.01(dd)	RuH^a	J_{HP} 11 J_{HH} 3.5

[a] In cyclohexane. [b] In $CDCl_3$ unless stated otherwise. [c] N.m.r. in $CD_3C_6D_5$ at −30 °C; the CH_2 signal appears as an asymmetric multiplet interpreted as an AB part of an ABX spectrum. In CD_3COCD_3 the A and B components are well separated. At 140 °C the CH_2 signal is a sharp doublet and the hydride signal has changed from a doublet at −30 °C to a 1 : 2 : 1 triplet ($J_{obs.}$ = 1.5 Hz) at 140 °C. [d] N.m.r. in $CD_3C_6D_5$ at 25 °C; no coalescence behaviour up to 70 °C. A gradual downfield shift with increasing temperature of all the signals is observed for both (6) and (7).

of the terminal alkyne $HC{\equiv}CCH_2NMe_2$, including a single-crystal *X*-ray determination of the structure of $[Ru_3H(CO)_9(Me_2NCCCH_2)]$. Note that, since the starting aminoalkyne has a CH_2 group isolating the alkyne from the nitrogen atom, an *sp* or sp^2 carbon atom would need to be incorporated adjacent to nitrogen to get effects like those seen by Shapley *et al.*[6]



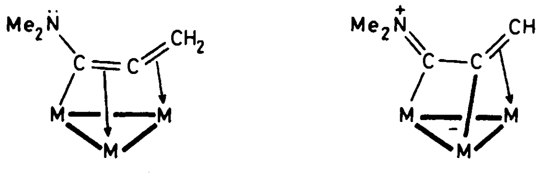
(6) M = Ru
(7) M = Os

Scheme 1.

Results and Discussion

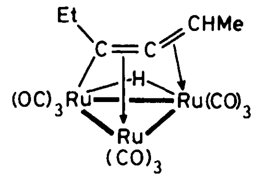
Synthesis and Characterisation of 3-*Dimethylaminoprop*-1-*yne Derivatives.*—Dodecacarbonyltriruthenium reacts readily with $HC{\equiv}CCH_2NMe_2$ in refluxing cyclohexane and after 1 h no starting carbonyl remains; a considerable amount of a red-maroon precipitate is formed, while the solution remains yellow-brown. The precipitate was incompletely characterised but from i.r. and ^1H n.m.r. evidence it appears to be a mixture of isomers of the well known type, $[Ru_2(alkyne)_2(CO)_6]$, in which the two alkynes have coupled to give a ruthenacyclopentadiene ring. Dinuclear species of this type are usually formed in reactions of alkynes with $[Ru_3(CO)_{12}]$ and isomers differing in the orientations of the coupled alkynes are commonly formed from unsymmetrical alkynes. The yellow-brown solution, however, gave on chromatography (t.l.c.; SiO_2) a low yield (7—8%) of a trinuclear complex (6) (Scheme 1). The osmium analogue, compound (7), is formed similarly from $[Os_3(CO)_{12}]$ (10%), but the reaction requires higher temperatures (refluxing heptane or octane).

The mass spectrum of complex (6) established the molecular formula $[Ru_3(CO)_9L]$ where L is the alkyne $HC{\equiv}CCH_2NMe_2$. Compounds (6) and (7) are hydrido-species but are not the complexes $[M_3H(CO)_9(\mu_3\text{-}C{\equiv}CCH_2NMe_2)]$, (1; R = CH_2NMe_2), even though compounds of type (1) are the normal products from reactions between $[M_3(CO)_{12}]$ and terminal alkynes. The i.r. spectra of compounds (6) and (7) around 2 000 cm^{-1} show eight or nine $\nu(CO)$ absorptions (Table 1) so that their symmetry must be lower than that of compound (1). Furthermore the ^1H n.m.r. spectrum shows non-equivalent CH_2 protons and NMe_2 groups. Coupling between the hydride and one of the CH_2 protons in compound (6) implies that the CH_2 group is bonded directly to the metal and hence the NMe_2 group must have migrated from this site. It has not migrated to the metal atoms to give $[M_3H(CO)_9(\mu\text{-}NMe_2)(\mu_3\text{-}C{=}C{=}CH_2)]$ which would be analogous to the formation of $[M_3H(CO)_9(\mu\text{-}OH)(\mu_3\text{-}C{=}C{=}CPh_2)]$ (M = Ru or Os) from $[M_3H(CO)_9(\mu_3\text{-}C{\equiv}CCPh_2OH)]$;[2] this compound is quite different spectroscopically from (6)



(A) (B)

Figure 1. Alternative modes of bonding considered for the compounds $[M_3H(CO)_9(Me_2NCCCH_2)]$, (6; M = Ru) and (7; M = Os)



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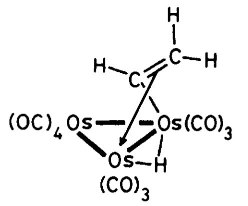

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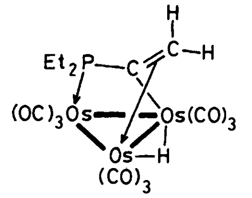

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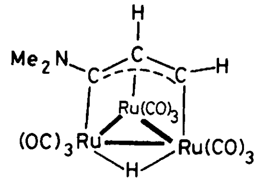
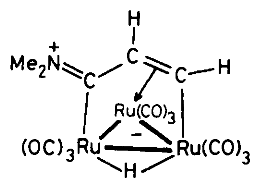


(11a)



(11b)

and (7). On spectroscopic evidence we favoured structure (A) for compounds (6) and (7) (Figure 1), related to that of compound (8) (*X*-ray structure [8]). Since the ν(CO) absorptions are around 11—20 cm^{-1} lower than for compounds of type (8), we thought that π donation from the NMe_2 group had caused an increase in polarity and a rise in the energy of the metal-centred orbitals. This is equivalent to saying that there is some contribution from form (B) in the ground-state structures of compounds (6) and (7). Expecting to find minor structural differences between compounds (6) and (8) which might be correlated with some contribution from the form (B), we carried out a single-crystal *X*-ray structure determination of $[Ru_3H(CO)_9(Me_2NCCCH_2)]$, compound (6).

X-*Ray Structure of* $[Ru_3H(CO)_9(Me_2NCCCH_2)]$ (6).—The molecular structure of compound (6) is shown in Figure 2, while selected interatomic distances and bond angles are given in Table 2 and Figure 3. It is clear that there has been a 1,3 shift of the NMe_2 group in forming compound (6) from $HC{\equiv}CCH_2NMe_2$. Furthermore description (B) is a better representation of the structure than (A). The carbon atom C(3) is bound to only one ruthenium atom, Ru(2). The short C(3)–N(4) bond length of 1.303(5) Å requires considerable C–N multiple bonding and consistent with this is the planarity at C(3) and N(4) (the sums of bond angles at these atoms are 359.4 and 359.9° respectively). It is worth comparing the structures of compounds (6) and (8) (Figure 3) since compound (8) has a structure corresponding to (A). The overall manner in which the μ_3 ligands are bound is similar but the C(3)–Ru(3) bond length of 2.261(5) Å in (8) has expanded to the non-bonding distance of 2.849(6) Å in (6). This allows the ligand to move into a more vertically aligned position in compound (6) so that the Ru(1)–Ru(2)–C(3) and Ru(3)–Ru(2)–C(3) angles are 74.1(2) and 70.2(2)° in (6) but 72.3(2) and 54.0(2)° in compound (8). The distances C(1)–C(2) and C(2)–C(3) are identical in compound (8) [1.369(8) and 1.365(8) Å respectively] and as expected for bonding description (B) these are rather different in compound (6) [1.394(6) and 1.439(5) Å respectively]. Since C(2)–C(3) is the central bond of a heterodiene system it is shorter than a normal single bond. Another significant difference between compounds (6) and (8) is the C(1)–C(2)–C(3) angle which is 127.4(4) Å in (6) and 142.3(6) Å

Table 2. Selected interatomic distances (Å) and angles (°) for compound (6)

Ru(1)–Ru(2)	2.861(1)	C(3)–N(4)	1.303(5)
Ru(2)–Ru(3)	2.787(1)	C(42)–N(4)	1.471(6)
Ru(1)–Ru(3)	2.849(1)	C(41)–N(4)	1.467(6)
Ru(1)–C(carbonyl)	1.899(5)—1.935(6)		
Ru(2)–C(carbonyl)	1.892(6)—1.936(6)		
Ru(3)–C(carbonyl)	1.884(6)—1.926(6)		
Ru(1)–H(1)	1.77(4)		
Ru(3)–H(1)	1.90(4)		
Ru(3)–Ru(1)–Ru(2)	58.4(1)	Ru(1)–C(2)–C(3)	107.6(3)
Ru(2)–Ru(3)–Ru(1)	61.0(1)	Ru(1)–C(2)–C(1)	72.9(3)
Ru(3)–Ru(2)–Ru(1)	60.5(1)	Ru(1)–C(1)–C(2)	71.4(3)
Ru(2)–C(3)–N(4)	137.1(2)	Ru(1)–C(2)–Ru(3)	81.7(2)
Ru(3)–C(2)–C(3)	106.4(3)	Ru(3)–C(2)–C(1)	125.0(3)
C(2)–C(3)–N(4)	123.6(4)	C(3)–N(4)–C(41)	121.9(4)
C(3)–N(4)–C(42)	123.9(4)	C(41)–N(4)–C(42)	114.1(4)

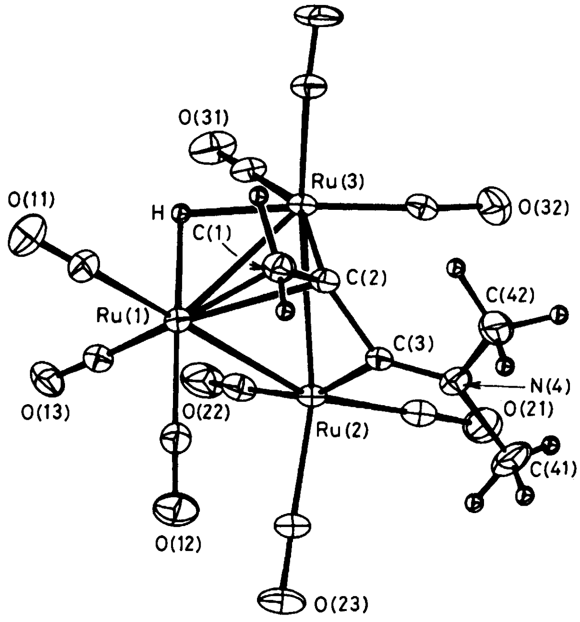
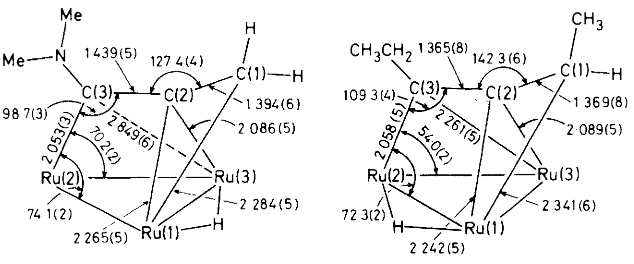


Figure 2. Molecular structure of $[Ru_3H(CO)_9(Me_2NCCCH_2)]$ (6)



(6) (8)

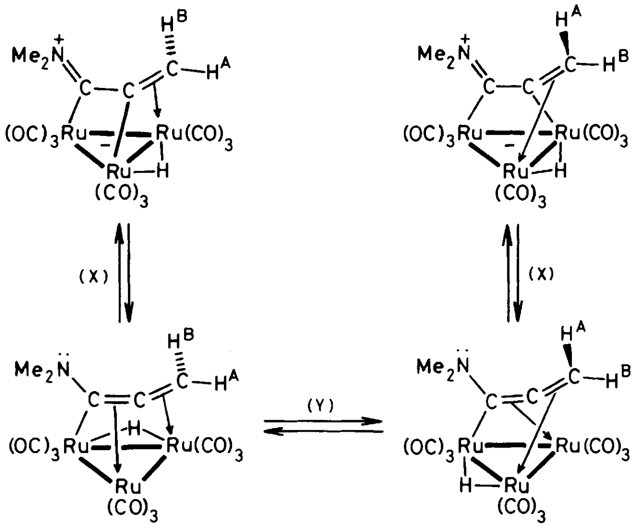
Figure 3. Diagrammatic representations of [$Ru_3H(CO)_9(Et\text{-}C{=}C{=}CHMe)$] (8) and of [$Ru_3H(CO)_9(Me_2NCCCH_2)$] (6) to show structural similarities and differences [CO groups omitted; distances(Å), angles(°)]

in (8), the larger angle being more consistent with an alleny description.

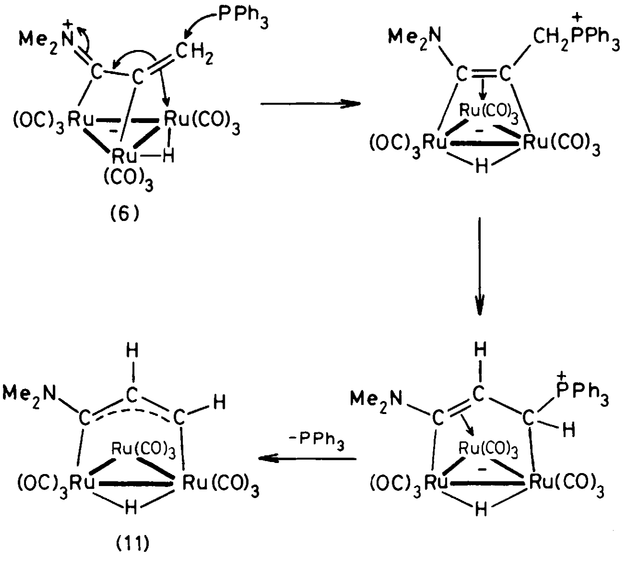
Apart from the differences in attachment of the μ_3 ligand, the hydride ligands bridge different metal atoms in the two compounds. The hydrogen atoms were located directly in both structures although their positions are, of course, only determined imprecisely. Since the hydride in (6) bridges Ru(1) and Ru(3), a direct structural analogy can be made between (6) and [$Os_3H(CO)_{10}(CH{=}CH_2)$], compound (9) (*X*-ray and neutron-diffraction structures[9]) and [$Os_3H(CO)_9(Et_2PC{=}CH_2)$], compound (10).[10] Indeed the geometries around Ru(1) and Ru(3) in compound (6) are very similar to those in compounds of type [$M_3H(CO)_{10}(\mu\text{-}X)$] (where X is a one- or two-atom bridge) such as (9). The hydride lies well below the metal plane, very close to the intersection of the C(12)–Ru(1) and C(32)–Ru(3) vectors. The two CO ligands *trans* to the hydride lie well above the metal plane. In contrast the hydride ligand in (8) is almost in the metal plane.

Fluxional Behaviour of [$Ru_3H(CO)_9(Me_2NCCCH_2)$] (6).—Compounds (6), (9), and (10) all show fluxionality with motions of the bridging organic ligands. The μ-vinyl group in compound (9) oscillates between the Os atoms it bridges and the vinyl component of the μ_3 ligand in compound (10) behaves similarly. These motions do not result in exchange of the non-equivalent geminal CH_2 protons. In compound (6), however, the geminal protons do exchange. At 30 °C and below the ^1H n.m.r. signals for these protons are overlapping multiplets appearing as the AB part of an ABX spectrum (X being the hydride nucleus). Only one of the CH_2 protons appears to couple with the hydride which consequently gives a doublet (δ -23.25, $J = 2.7$ Hz). At 85 °C and above the CH_2 multiplets simplify into a doublet, becoming sharp and well resolved at 130 °C and above ($J_{obs.} = 1.5$ Hz). At these higher temperatures the hydride signal is a 1 : 2 : 1 triplet ($J_{obs.} = 1.5$ Hz) so that a time-averaged A_2X system has developed and the non-equivalent CH_2 protons are rapidly exchanging and couple equally to the hydride ligand. The average coupling constant observed at 140 °C (1.5 Hz) should be half the observed low-temperature coupling constant (2.7 Hz), but a small unresolved coupling between the second CH_2 proton and the hydride of 0.3 Hz would account for the averaged coupling observed.

By analogy with compounds (9) and (10), a direct vinyl oscillation in the zwitterionic form of (6) would maintain the *cis* and *trans* relations of H^A and H^B with respect to the Ru–C σ bond and could not account for their interchange (Scheme 2). We believe that processes (X) and (Y) are the best explanations. Relatively minor geometric changes are involved in (X) while (Y) has been well established as a rapid process for [$Ru_3H(CO)_9(\mu_3\text{-}MeC{=}C{=}CMe_2)$].[11] The difference between compound (6) and compounds (9) and (10) is that the plane of the vinyl group approaches an orientation parallel to the metal plane in (6) but perpendicular in the transition states for (9) and (10). We cannot rule out a separate process with a transition state having a vertical vinyl orientation for (6) since this would not be observable in our measurements.



Scheme 2.



Scheme 3.

The NMe_2 groups give two singlets even at 140 °C although these start to broaden at this temperature with the onset of exchange (estimated $T_c > 150$ °C). Although accurate rate data were unobtainable, it would seem that processes (X) and (Y) (Scheme 2) occur without rotation about the C–N bond so there must be sufficient multiple C–N bonding in the allenyl form illustrated to prevent methyl exchange.

Mechanism of Formation of Compounds (6) *and* (7).—We have no direct observations to support the mechanism of formation of these compounds. However, terminal alkynes have a strong tendency to give compounds of type (1) so we may presume that compounds (1; R = CH_2NMe_2) are

Table 3. Atom co-ordinates ($\times 10^4$) for compound (6)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ru(1)	2 229(0.5)	949(0.5)	4 786(0.5)	C(23)	1 545(3)	2 839(3)	6 495(3)
Ru(2)	2 900(0.5)	2 775(0.5)	6 280(0.5)	O(23)	752(2)	2 893(3)	6 619(2)
Ru(3)	4 310(0.5)	2 242(0.5)	5 363(0.5)	C(31)	5 427(3)	1 215(4)	6 288(2)
C(11)	1 855(3)	−344(3)	3 818(3)	O(31)	6 052(3)	548(3)	6 807(2)
O(11)	1 622(3)	−1 128(3)	3 269(2)	C(32)	4 973(3)	3 817(4)	5 886(3)
C(12)	750(3)	1 283(3)	4 663(3)	O(32)	5 396(3)	4 760(3)	6 191(2)
O(12)	−134(2)	1 509(3)	4 580(2)	C(33)	4 880(3)	2 149(3)	4 396(3)
C(13)	2 492(2)	−228(3)	5 791(2)	O(33)	5 237(4)	2 175(3)	3 835(3)
O(13)	2 623(2)	−990(2)	6 348(2)	C(1)	2 073(3)	2 423(4)	3 652(2)
C(21)	3 593(3)	4 169(3)	7 074(2)	C(2)	2 746(3)	2 937(3)	4 515(2)
O(21)	3 991(3)	5 006(3)	7 548(2)	C(3)	2 431(2)	3 833(3)	5 074(2)
C(22)	3 689(3)	1 555(3)	7 252(2)	N(4)	2 093(2)	5 001(3)	4 809(2)
O(22)	4 220(3)	908(3)	7 858(2)	C(41)	1 820(6)	5 900(5)	5 415(4)
				C(42)	2 028(4)	5 566(4)	3 922(3)

formed initially but isomerise to (6) or (7) (Scheme 1). The α-carbon atoms of compounds of type (1) are electrophilic and are attacked by various nucleophiles intramolecularly[3] or intermolecularly.[12] Furthermore the NMe_2 group in these alkynyl intermediates would be insulated by the CH_2 group and would be nucleophilic. The NMe_2-group migration is therefore to be expected but could occur by an intramolecular 1,3 shift or alternatively intermolecularly, possibly in a concerted bimolecular manner.

Isomerisation of Compound (6) *catalysed by* PPh_3.—Compound (6) is quite stable at 140 °C in [$^2H_8$]toluene in a sealed n.m.r. tube; there are no signs of isomerisation as, for example, in the conversion of the allenyl compound [$Ru_3H(CO)_9(EtC{=}C{=}CH_2)$] into the allyl-type compound [$Ru_3H(CO)_9(EtCCHCH)$] which occurs below 100 °C.[13] However, treatment of compound (6) with PPh_3 in cyclohexane for only 20 min at 55 °C gave a significant amount (20%) of the isomer [$Ru_3H(CO)_9(Me_2NCCHCH)$] (11) as well as a similar amount of the substitution compound [$Ru_3H(CO)_8(PPh_3)(Me_2NCCCH_2)$] (12). Co-ordination of PPh_3 at ruthenium with displacement of CO would no doubt be irreversible under these conditions so that the isomerisation must occur by attack at the organic ligand. We expect the terminal CH_2 group of compound (6) to be electrophilic; note that [$Os_3H(CO)_9(MeC{=}C{=}CH_2)$] readily gives [$Os_3H(CO)_9(MeC{=}CCH_2PMe_2Ph)$] on addition of PMe_2Ph.[12] Hence we propose a mechanism like that shown in Scheme 3. The CH_2 hydrogen atoms adjacent to the phosphonium centre would be quite acidic and a deprotonation–protonation route to compound (11) is feasible although the precise nature of the intermediates is uncertain.

Experimental

Reaction of [$Ru_3(CO)_{12}$] *with* 3-*Dimethylaminoprop*-1-*yne*.—A solution of [$Ru_3(CO)_{12}$] (0.500 g) and $HC{\equiv}CCH_2NMe_2$ (0.1 cm^3) in cyclohexane (250 cm^3) was heated under reflux for 1 h. An abundant red-maroon precipitate was separated which gave broad i.r. absorptions centred at 2 048 and 1 982 cm^{-1} and a complicated ^1H n.m.r. spectrum in CD_3OD or CD_3COCD_3. This material was not further characterised but is probably an isomeric mixture of dinuclear compounds. The yellow-brown filtrate was evaporated to dryness and separated by chromatography [t.l.c. on SiO_2; eluant, light petroleum (b.p. 40—60 °C)–diethyl ether (5 : 1 v/v)] to give a single yellow band which gave [$Ru_3H(CO)_9(Me_2NCCCH_2)$] (6) (7—8%) as yellow crystals. The compound was characterised by its mass spectrum (parent molecular ion), i.r. and ^1H n.m.r. spectra, and a single-crystal *X*-ray structure determination.

Reaction of [$Os_3(CO)_{12}$] *with* 3-*Dimethylaminoprop*-1-*yne*.—A solution of [$Os_3(CO)_{12}$] (0.300 g) and $HC{\equiv}CCH_2NMe_2$ (0.102 g) in heptane (150 cm^3) was heated under reflux for 12 h. After removal of the solvent *in vacuo*, the orange-yellow residue was separated by t.l.c. on SiO_2 (eluant: pentane–diethyl ether, 10 : 3 v/v) to give several bands. The main yellow band gave [$Os_3H(CO)_9(Me_2NCCCH_2)$] (7) (0.031 g) as yellow crystals characterised by its i.r. and ^1H n.m.r. spectra (Found: C, 18.4; H, 1.2; N, 1.5. $C_{14}H_9NO_9Os_3$ requires C, 18.55; H, 1.0; N, 1.55%). The other bands gave very small quantities of compounds which were not characterised. A similar reaction occurs in refluxing octane (2 h).

Reaction of [$Ru_3H(CO)_9(Me_2NCCCH_2)$] (6) *with* PPh_3.—A solution of compound (6) (0.05) g in cyclohexane was treated with PPh_3 (0.03 g) at 55 °C for 20 min. Chromatographic work-up gave two yellow products. The first was characterised as [$Ru_3H(CO)_9(Me_2NCCHCH)$], compound (11) (20%), which is an isomer of compound (6) and characterised by its mass spectrum (parent molecular ion) and its i.r. and ^1H n.m.r. spectra, particularly in comparison with those of [$Ru_3H(CO)_9(Me_2NCCHCMe)$].[7] The second yellow product is [$Ru_3H(CO)_8(PPh_3)(Me_2NCCCH_2)$], compound (12) (20%), a PPh_3-substituted derivative of (6), on the basis of its i.r. and ^1H n.m.r. spectra (Table 1).

Crystal Structure Determination for [$Ru_3H(CO)_9(Me_2NCCCH_2)$] (6).—*Crystal data.* $C_{14}H_9NO_9Ru_3$, $M = 638.44$, monoclinic, $a = 13.067(2)$, $b = 10.398(2)$, $c = 15.544(2)$ Å, $\beta = 112.78(2)°$, $U = 1\,947.3$ Å^3, space group $P2_1/n$ (alternative no. 14, $P2_1/c$), $Z = 4$, $D_c = 2.18$ g cm^{-3}, $\mu(\text{Mo-}K_\alpha) = 21.22$ cm^{-1}, $F(000) = 1\,216$.

Data collection. A Nonius CAD4 diffractometer was used with graphite-monochromatised Mo-K_α radiation ($\lambda = 0.710\,69$ Å), and the ω—2θ scan mode; 3 875 data were measured ($1.5 \leqslant \theta \leqslant 25.0°$; $h,k,\pm l$) of which 3 426 were unique and 3 138 considered observed [$I > 1.5\sigma(I)$]. The data were corrected for absorption empirically.[14]

Structure solution. The structure was solved by direct methods (3Ru atoms), developed by routine procedures, and atomic parameters were refined by full-matrix least-squares methods. Non-hydrogen atoms were assigned anisotropic thermal parameters and hydrogen atoms were freely refined with individual isotropic thermal parameters. The final *R* and *R′* values were 0.019 8 and 0.023 with reflection weights of $w = 1/[\sigma^2(F_o) + 0.003|F_o|^2]$ and the number of parameters varied was 280. The final atomic co-ordinates are given in Table 3. Programs, computers, and sources of scattering factor data are as given in ref. 15.

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References

1 M. I. Bruce, in 'Comprehensive Organometallic Chemistry,' eds. G. Wilkinson, F. G. A. Stone, and E. W. Abel, Pergamon Press, Oxford, 1982, ch. 32.5, p. 843; R. D. Adams and J. P. Selegue, *ibid.*, ch. 33.3, p. 1023.

2 S. Aime, A. J. Deeming, M. B. Hursthouse, and J. D. J. Backer-Dirks, *J. Chem. Soc., Dalton Trans.*, 1982, 1625.

3 S. Aime and A. J. Deeming, *J. Chem. Soc., Dalton Trans.*, 1983, 1807.

4 S. Ermer, R. Karpelus, S. Miura, E. Rosenberg, A. Tiripicchio, and A. M. Manotti Lanfredi, *J. Organomet. Chem.*, 1980, **187**, 81.

5 B. E. Hanson, B. F. G. Johnson, J. Lewis, and P. R. Raithby, *J. Chem. Soc., Dalton Trans.*, 1980, 1852.

6 J. R. Shapley, M. Tachikawa, M. R. Churchill, and R. A. Lashewycz, *J. Organomet. Chem.*, 1978, **162**, C39; M. R. Churchill and R. A. Lashewycz, *Inorg. Chem.*, 1979, **18**, 848.

7 S. Aime, G. Jannon, D. Osella, and A. J. Deeming, *J. Organomet. Chem.*, 1981, **214**, C15.

8 G. Gervasio, D. Osella, and M. Valle, *Inorg. Chem.*, 1976, **15**, 1221.

9 A. G. Orpen, A. V. Rivera, E. G. Bryan, D. Pippard, G. M. Sheldrick, and K. D. Rouse, *J. Chem. Soc., Chem. Commun.*, 1978, 723; A. G. Orpen, D. Pippard, G. M. Sheldrick, and K. D. Rouse, *Acta Crystallogr., Sect. B*, 1978, **34**, 2466.

10 A. J. Deeming, *J. Organomet. Chem.*, 1977, **128**, 63.

11 S. Aime, R. Gobetto, D. Osella, L. Milone, and E. Rosenberg, *Organometallics*, 1982, **1**, 640.

12 K. Henrick, M. McPartlin, A. J. Deeming, S. Hasso, and P. J. Manning, *J. Chem. Soc., Dalton Trans.*, 1982, 899.

13 O. Gambino, M. Valle, S. Aime, and G. A. Vaglio, *Inorg. Chim. Acta*, 1974, **8**, 71; M. Evans, M. Hursthouse, E. W. Randall, E. Rosenberg, L. Milone, and M. Valle, *J. Chem. Soc., Chem. Commun.*, 1972, 545.

14 A. C. T. North, D. C. Phillips, and F. S. Mathews, *Acta Crystallogr., Sect. A*, 1968, **24**, 351.

15 M. B. Hursthouse, R. A. Jones, K. M. A. Malik, and G. Wilkinson, *J. Am. Chem. Soc.*, 1979, **101**, 4128.

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